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14. ABSTRACT

The principal investigators have developed new and innovative methods for the preparation of catalytic systems consisting of very small metal clusters supported on an oxide and for the preparation of nano-structured oxides for supporting catalysts or for performing catalysis. Theory was used to analyze many of the observations or to propose new catalytic systems.

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Catalysis by Nanostructures: Methane, Ethylene Oxide, and Propylene Oxide Synthesis on Ag, Cu or Au nanoclusters, F49620-01-1-0459
Final Performance Report (for the period 07/01/01 - 08/31/07)

A major effort of the group was the design, construction, and use of a new instrument in which we can deposit mass-selected clusters on a surface in ultra-high vacuum and perform scanning tunneling microscopy (STM), Auger spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermal desorption measurements¹⁻¹⁸. This instrument is still unique in the world; there are very few groups that perform catalysis work with mass-selected clusters and ours is the only one that can image the clusters *in situ*, before and after performing catalysis on them. This is important because the clusters may migrate on the surface and merge to make larger clusters. STM allows us to work under conditions when such migration does not take place so that the integrity of the clusters is preserved.

The instrument has been described in the literature¹¹. Experiments determining the structure and the mobility of Ag clusters and Au clusters on TiO₂(110) have been published^{1-3,14-16}. We found that Au atoms are very mobile and form large clusters at room temperature if the surface has hydroxyls on it. The mobility is lost if the surface is cleaned by heating to about 600 K to remove the hydroxyls and make oxygen vacancies on the surface. The Au₂ to Au₇ clusters are not mobile on the time scale of the experiments. The structure of the clusters has been established by a combination of STM and theory. It was found that the structure of the adsorbed clusters is different from that of the same clusters in the gas phase, indicating a strong interaction with the support. It is also interesting that in gas phase the clusters are planar but on the surface they are three-dimensional when they have five atoms or more.

Density functional theory was used to provide a better understanding of these systems. Here are a few of the highlights. Gold atoms are mobile and prefer to bind to oxygen vacancies¹⁸. It has been proposed repeatedly in the literature that Au clusters bind at the site of oxygen vacancies and take electrons from them and that this is what makes them active as oxidation catalysts. We found that, for Au clusters on TiO₂, this is true only for Au₁, Au₃, Au₅ and Au₇ and for certain Au strips on the surface⁵. We have explained the charge exchange between the cluster and the surface from the properties of the molecular orbitals. We also discovered⁸ a very striking effect: the binding energy of an oxygen or Au atom to the titania surface can be very strongly modified by coadsorption with Au, Au₃, Au₅, Au₇ or hydroxyls. Moreover all these molecules affect oxygen or Au binding by the same amount. We showed that they all act by donating electrons in the conduction band and oxygen or gold uses these electrons to form a strong bond. In other papers we have analyzed thoroughly the nature of the bonds between a variety of Au clusters and the stoichiometric surface of titania⁶, a defective titania surface⁷ and a surface having hydroxyls on it⁹.

Previous studies of oxidation catalytic reactions neglected the role of spin. We have shown¹⁰ that spin conservation during a catalytic reaction is very important. Experiments have revealed that O₂ dissociates at the site of an oxygen vacancy on the surface of TiO₂. Previous density functional calculations found that the activation energy for dissociation is very high, disagreeing with the experiments. We have shown that if the potential energy surface is calculated by

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imposing spin conservation, the activation energy is consistent with the experiments. We expect this paper to have a substantial impact on the theory of catalytic oxidation.

Small Au clusters are good catalysts while bulk Au is inert. This has been discussed extensively in the literature. We performed calculations that show that the activity is due to what we call "orbital roughness": the HOMO and the LUMO of small clusters protrude outside the cluster and provide good binding sites for oxygen, CO, propene and other molecules. We emphasize that orbital roughness is distinct from the geometric roughness by giving examples where the least-coordinated atoms are not the most active since no frontier orbital protrudes from them. We showed that this qualitative idea works for solid surfaces¹² and for several gas phase systems^{1-3,14-16}.

There have been reports in the literature that in some catalytic reaction the catalyst is not the neutral Au but an ionic species. We have performed calculations that show that when a Au atom replaces a Ti atom on the surface of TiO₂, the oxide becomes active for CO oxidation. We believe that such doped oxides are very promising catalysts and are pursuing this topic further.

Wilson Ho's group reported at an AFOSR meeting some very intriguing results on supported, linear Au clusters that seemed to violate the Pauli principle. We have shown that if the results are properly interpreted, there is no such violation¹³.

Finally, we have studied the surface structure of γ -alumina and determined the likely position of the missing atoms in the spinel structure¹⁷.

The behavior of Au and Ag clusters in gas phase. One of the interesting and sometimes controversial topics in catalysis is the role of the support on which the metallic catalyst resides. To understand this we studied the chemistry of gas-phase clusters to compare it to that of supported clusters. The experiments, accompanied by theory, determined with high accuracy the binding energies of various molecules to Ag clusters of various sizes¹⁹⁻²³ and discovered many interesting chemical phenomena and regularities in the dependence of chemistry on the size of the clusters and the number of ligands. We also documented an interesting phenomenon: chemisorption of a molecule on a cluster can change its shape dramatically. This finding gives an important warning to theorists who determine the ground state geometry of the cluster and then assume that the molecule will distort it slightly upon adsorption. In some cases this calculation leads to high-energy isomers and misses the real structure of the system. Our group has also performed a large number of calculations to determine the nature of the bonding of hydrogen, oxygen, and propene. These calculations used high-level quantum chemistry methods for small clusters and density functional theory for large clusters. We proposed simple rules for finding the binding sites and determining trends in binding energy for oxygen and propene on Au and AuAg clusters²⁴⁻³².

Catalysis on supported metal clusters. In parallel with the work in ultra-high vacuum, we performed research on catalysis under high-pressure conditions with metal clusters deposited on high-surface-area supports, of the kind used in industry. One preparation route involved using micelles to make metal clusters surrounded by an organic layer³³⁻³⁹. The micelles are deposited on a support and used as catalysts. The method of synthesis is such that one can achieve good

size control. This is important since it is becoming apparent that catalytic activity depends on the size of the catalyst particles.

Gold nanoparticles synthesized by micelle encapsulation were dip-coated on a solid to produce a quasi-regular array of Au nanoparticles (diameter 1.3 - 4. nm) with tight control of particle size. This method can be applied to deposit Au on any substrate. The material was used to determine the dependence of the rate of CO electro-oxidation on the size of the Au particles^{36,37} and the nature of the support. In a further study⁴⁰ we determined the dependence of the kinetics of electrocatalytic oxygen reduction in basic electrolyte, on the size of Au nanoparticles (3 nm and 7 nm) supported on carbon. The size-selected nanoparticles were prepared by reverse micelle encapsulation in diblock copolymers and the kinetic current for oxygen reduction was measured with a rotating disk electrode. The kinetic current was found to be 3 times higher for the 3-nm gold nanoparticles compared to the 7-nm gold nanoparticles at 23°C. The 3-nm particles facilitate four-electron electro-reduction whereas a two-electron reduction was inferred from the RDE data on the 7-nm particles. From experiments of the temperature-dependent current, the apparent activation energy for the 3-nm clusters was found to be half that of the 7-nm clusters (0.1 eV and 0.2 eV, respectively).

Gold clusters of varying diameters (8-22 nm) were prepared by reducing a Au salt, and encapsulating the Au nanoparticles formed in a polymer³³. A variety of high area oxides (TiO₂, ZnO, ZrO₂, SiO₂) were impregnated with the clusters and calcined. We studied how sintering of the clusters and their activity to CO oxidation and propene hydrogenation depended on the support. We found that Au is most active when supported on TiO₂. We have also shown that Au particles made by synthesis in micelles with size control and deposited on TiO₂ are very good room-temperature propylene epoxidation catalysts³⁴. In another study³⁵ we discovered that Pd nanoclusters form benzene from propylene and oxygen at 70 °C. This reaction does not take place on large Pd clusters or on Pd-organometallic complexes.

Gold nanoclusters were successfully deposited in the interior of alumina nanotubes fabricated as ordered arrays⁴¹ and coated with TiO₂. A pressure impregnation process was used to inject the titania and Au precursors into mesoporous alumina. After thermal treatment, Au nanoclusters were well-dispersed on the interior walls of nanotubular TiO₂. The TiO₂ nanotubes were shown by x-ray diffraction to be entirely anatase. Transmission electron microscopy imaging confirmed that 80% of the Au particles were 4.1 nm±2.0 nm in diameter. This material exhibited catalytic CO oxidation activity at low temperatures, and the approach is a useful fabrication platform for miniature planar fuel cells, gas sensors, and heterogeneous catalysts. In addition, the coarsening of Au in this nano-tubular array is reduced. In another attempt to reduce sintering we showed that Au particles are stabilized when deposited on TiO₂ whose surface was roughened by sputtering⁴². We have also observed that Au clusters deposited on either silica or hydrogen terminated silicon substrates will coarsen if exposed to UV radiation. We were unable to find any explanation for this phenomenon, which is not due to heating of the substrate by radiation.

To connect the work performed in UHV to that performed under realistic catalytic reactions, we designed, fabricated, and tested a microreactor in which we can place a single-crystal surface with metal clusters on it and perform high-pressure catalysis⁴³. Because samples prepared in ultra-high vacuum contain a very small amount of catalyst, it is critical the microreactor had a

very small volume above the catalyst and a very small “dead space” between the reaction chamber and the mass spectrometer. After an epic battle with leaks and after trying many different materials, we managed to make a working reactor. We plan to use it to study the catalytic properties of the mass-selected clusters prepared in the UHV system.

We used micelle synthesis to prepare Au-Pd nanoclusters and characterize them by high-resolution TEM³⁹. We found that in the presence of air, the Pd segregates at the surface of the cluster, making a Pd shell with a Au core. We are now studying the ability of these clusters to selectively perform the hydrogenation of acetylene to ethylene. This is an important reaction because acetylene must be removed from the ethylene stream before fabricating polyethylene.

The gas-phase oxidation of CO catalyzed by iridium⁴⁴ was studied under CO-rich reactant conditions, over a large pressure range, to investigate the controversial size and pressure dependence. The reactivity of iridium clusters with an average size of 3 nm was compared to macroscopic metal particles with extended single crystal facets over a range of temperatures (433 – 573 K). The apparent activation energies for CO oxidation were consistent with the known activation energies for CO desorption from iridium surfaces. No size-specific dependence of the reaction kinetics was measured and no indication of the previously reported “pressure gap” was observed.

Hydrogen is added to oxygen and propylene in the synthesis of propylene oxide catalyzed by Au supported on TiO₂. The reason for using hydrogen in an oxidation reaction is not clear. We studied⁴⁵ the adsorption and desorption of hydrogen on TiO₂ to try to add to our knowledge of this system. The results were consistent with DFT calculations.

Catalytic properties of nanostructured oxides. Nanostructured oxides are used as supports, as catalysts and as materials for sensors. Recent research shows that the chemistry of the oxides depends very substantially on their size. Oxides with a very large surface-to-volume ratio perform chemistry that does not take place on a more coarse material with the same chemical composition. Our group has managed to prepare very thin oxide nanowires and study their properties⁴⁶⁻⁵⁴. One of the most significant findings is that one can control the activity of SnO₂ to CO oxidation by placing a SnO₂ nanowire above a gate and adding or removing electrons in the wire. This work was inspired by calculations¹² that showed that adding an electron to a slab of Au increases, substantially, its ability to adsorb oxygen and weaken the O-O bond. We have also showed that the sensing ability of a SnO₂ nanowire is substantially enhanced when we deposit Pd clusters on the wire⁴⁶. This happens because Pd clusters dissociate O₂, which spills over on the oxide, annihilating the oxygen vacancies at the surface and lowering substantially and rapidly the conductivity of the wire.

Three articles were written⁵⁵⁻⁵⁷ on the fabrication of Au nanostructures on which surface-enhanced Raman signals are so strong that one can detect Raman spectra from a single molecule. Two others^{58,59} present a novel synthesis of highly ordered composite mesostructured nanowires with various degrees of physical confinement. These can be used in catalysis or in fabrication of sensors. Finally we edited a special issue of the *Journal of Chemical Physics* for which we wrote an introduction⁶⁰.

Thirteen students partially or wholly supported by this project have received Ph.D. degrees⁶¹⁻⁷³: Erin S. Baker, 2005; Lauren Aubin Benz, 2007; Daniel Gargas, 2007; Thomas F. Jaramillo, 2004; Manuel J. Manard, 2006; Ryan M. Olson, 2007; Erin L. Orazem, 2007; Jason P. Schmidt, 2003; Donald J. Sirbuly, 2003; Mikhail Sushchikh, 2006; Burcin Temel, 2006; Sergey A. Varganov, 2005; Qiang Zhang, 2003. Three other graduate students are currently enrolled: Andrew Morrill, Bosiljka Njagic, and Wei Tang.

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1. L. Benz, X. Tong, P. Kemper, Y. Lilach, A. Kolmakov, H. Metiu, M. T. Bowers, and S. K. Buratto, Landing of size-selected Ag_n^+ clusters on single crystal $\text{TiO}_2(110)-(1 \times 1)$ surfaces at room temperature. *J. Chem. Phys.* 122, art. no. 081102 (2005)
2. L. Benz, X. Tong, P. Kemper, H. Metiu, M. T. Bowers, and S. K. Buratto, Pinning mononuclear Au on the surface of titania. *J. Phys. Chem. B* 110, 663-666 (2006)
3. S. K. Buratto, M. T. Bowers, H. Metiu, M. Manard, X. Tong, L. Benz, P. Kemper, and S. Chrétien, Au_n and Ag_n ($n = 1-8$) nanocluster catalysts: gas phase reactivity to deposited structures. In *The Chemical Physics of Solid Surfaces, vol. 12 of Atomic Clusters From Gas Phase to Deposited*, D. P. Woodruff, Ed. (Elsevier, 2006). Chapter 4, pp. 151-199
4. S. Chrétien and H. Metiu, Density functional study of the CO oxidation on a doped rutile $\text{TiO}_2(110)$: Effect of ionic Au in catalysis. *Catalysis Lett.* 107, 143-147 (2006)
5. S. Chrétien and H. Metiu, Density functional study of the charge on Au_n clusters ($n=1-7$) supported on a partially reduced rutile $\text{TiO}_2(110)$: Are all clusters negatively charged? *J. Chem. Phys.* 126, Art. No. 104701 (2007)
6. S. Chrétien and H. Metiu, Density functional study of the interaction between small Au clusters, Au_n ($n=1-7$) and the rutile TiO_2 surface. I. Adsorption on the stoichiometric surface. *J. Chem. Phys.* 127, Art. No. 084704 (2007)
7. S. Chrétien and H. Metiu, Density functional study of the interaction between small Au clusters, Au_n clusters ($n=1-7$) and the rutile $\text{TiO}_2(110)$ surface. II. Adsorption on a partially reduced surface. *J. Chem. Phys.* 127, art. no. 244708 (2007)
8. S. Chrétien and H. Metiu, Enhanced adsorption energy of Au_1 and O_2 on the stoichiometric $\text{TiO}_2(110)$ surface by co-adsorption with other molecules. *J. Chem. Phys.* to appear (2008)
9. S. Chrétien and H. Metiu, The interaction of Au_n ($n = 1-7$) with the $\text{TiO}_2(110)$ surface. III. Partially hydroxylated TiO_2 . *J. Chem. Phys.* to be submitted (2008)
10. S. Chrétien and H. Metiu, The role of spin in oxygen surface interactions: O_2 dissociation on reduced rutile $\text{TiO}_2(110)$. *J. Chem. Phys.* to be submitted (2008)
11. P. Kemper, A. Kolmakov, X. Tong, Y. Lilach, L. Benz, M. Manard, H. Metiu, S. K. Buratto, and M. T. Bowers, Formation, deposition and examination of size selected metal

- clusters on semiconductor surfaces: An experimental setup. *Intl J. Mass Spectrometry* 254, 202-209 (2006)
12. G. Mills, M. S. Gordon, and H. Metiu, Oxygen adsorption on Au clusters and a rough Au(111) surface: The role of surface flatness, electron confinement, excess electrons, and band gap. *J. Chem. Phys.* 118, 4198-4205 (2003)
 13. G. Mills, B. Wang, W. Ho, and H. Metiu, Electronic states of linear Au clusters supported on metal surfaces: Why are they like those of a particle in a box? *J. Chem. Phys.* 120, 7738-7740 (2004)
 14. X. Tong, L. Benz, S. Chrétien, P. Kemper, A. Kolmakov, H. Metiu, M. T. Bowers, and S. K. Buratto, Pinning mass-selected Ag_n clusters on the $\text{TiO}_2(110)$ -1X1 surface via deposition at high kinetic energy. *J. Chem. Phys.* 123, art. no. 204701 (2005)
 15. X. Tong, L. Benz, P. Kemper, H. Metiu, M. T. Bowers, and S. K. Buratto, Intact size-selected Au_n clusters on a $\text{TiO}_2(110)$ -(1 x 1) surface at room temperature. *J. Am. Chem. Soc.* 127, 13516-13518 (2005)
 16. X. Tong, L. Benz, A. Kolmakov, S. Chrétien, H. Metiu, and S. K. Buratto, The nucleation sites of Ag clusters grown by vapor deposition on a $\text{TiO}_2(110)$ -1 x 1 surface. *Surface Science* 575, 60-68 (2005)
 17. A. Vijay, G. Mills, and H. Metiu, Structure of the (001) surface of γ -alumina. *J. Chem. Phys.* 117, 4509-4516 (2002)
 18. A. Vijay, G. Mills, and H. Metiu, Adsorption of gold on stoichiometric and reduced rutile $\text{TiO}_2(110)$ surfaces. *J. Chem. Phys.* 118, 6536-6551 (2003)
 19. M. J. Manard, P. R. Kemper, and M. T. Bowers, Bonding interactions in $\text{Ag}^+(\text{O}_2)_n$ and $\text{Ag}^{2+}(\text{O}_2)_n$ clusters: experiment and theory. *Intl J. Mass Spectrometry* 228, 865-877 (2003)
 20. M. J. Manard, P. R. Kemper, and M. T. Bowers, Binding interactions of mono- and diatomic silver cations with small alkenes: experiment and theory. *Intl J. Mass Spectrometry* 241, 109-117 (2005)
 21. M. J. Manard, P. R. Kemper, and M. T. Bowers, Probing the structure of gas-phase metallic clusters via ligation energetics: sequential addition of C_2H_4 to Ag_m^+ ($m = 3-7$). *J. Am. Chem. Soc.* 127, 9994-9995 (2005)
 22. M. J. Manard, P. R. Kemper, and M. T. Bowers, An experimental and theoretical investigation into the binding interactions of silver cluster cations with ethene and propene. *Intl J. Mass Spectrometry* 249-250, 252-262 (2006)
 23. M. J. Manard, P. R. Kemper, C. J. Carpenter, and M. T. Bowers, Dissociation reactions of diatomic silver cations with small alkenes: experiment and theory. *Intl J. Mass Spectrometry* 241, 99-108 (2005)
 24. S. Chrétien, M. S. Gordon, and H. Metiu, Density functional study of the adsorption of propene on mixed gold-silver clusters, Au_nAg_m : Propensity rules for binding. *J. Chem. Phys.* 121, 9931-9937 (2004)
 25. S. Chrétien, M. S. Gordon, and H. Metiu, Density functional study of the adsorption of propene on silver clusters, Ag_m^q ($m=1-5$; $q=0,+1$). *J. Chem. Phys.* 121, 9925-9930 (2004)
 26. S. Chrétien, M. S. Gordon, and H. Metiu, Binding of propene on small gold clusters and on Au(111): Simple rules for binding sites and relative binding energies. *J. Chem. Phys.* 121, 3756-3766 (2004)

27. G. Mills, M. S. Gordon, and H. Metiu, The adsorption of molecular oxygen on neutral and negative Au_n clusters (n=2-5). *Chem. Phys. Lett.* 359, 493-499 (2002)
28. R. Olson, S. Varganov, M. S. Gordon, and H. Metiu, The binding of the noble metal cations Au⁺ and Ag⁺ to propene. *Chem. Phys. Lett.* 412, 416-419 (2005)
29. R. M. Olson, S. Varganov, M. S. Gordon, H. Metiu, S. Chrétien, P. Piecuch, K. Kowalski, S. A. Kucharski, and M. Musial, Where does the planar-to-nonplanar turnover occur in small gold clusters? *J. Am. Chem. Soc.* 127, 1049-1052 (2005)
30. S. A. Varganov, R. M. Olson, M. S. Gordon, and H. Metiu, The interaction of oxygen with small gold clusters. *J. Chem. Phys.* 119, 2531-2537 (2003)
31. S. A. Varganov, R. M. Olson, M. S. Gordon, G. Mills, and H. Metiu, Reply to a comment: Oxygen adsorption on Au clusters by W. T. Wallace, A. J. Leavitt, and R. J. Whetten. *Chem. Phys. Lett.* 368, 778-779 (2003)
32. S. A. Varganov, R. M. Olson, M. S. Gordon, G. Mills, and H. Metiu, A study of the reactions of molecular hydrogen with small gold clusters. *J. Chem. Phys.* 120, 5169-5175 (2004)
33. J. Chou, N. R. Franklin, S. H. Baeck, T. F. Jaramillo, and E. W. McFarland, Gas-phase catalysis by micelle derived Au nanoparticles on oxide supports. *Catalysis Lett.* 95, 107-111 (2004)
34. J. Chou and E. W. McFarland, Direct propylene epoxidation on chemically reduced Au nanoparticles supported on titania. *Chem. Commun.*, 1648-1649 (2004)
35. J. Chou, S. Y. Zhang, S. L. Sun, and E. W. McFarland, Benzene formation at 70 degrees C by coupling of propylene on supported Pd nanoclusters. *Angew. Chem. Intl Ed.* 44, 4735-4739 (2005)
36. T. F. Jaramillo, S. H. Baeck, B. Roldan Cuenya, and E. W. McFarland, Catalytic activity of supported Au nanoparticles deposited from block copolymer micelles. *J. Am. Chem. Soc.* 125, 7148-7149 (2003)
37. B. Roldan Cuenya, S. H. Baeck, T. F. Jaramillo, and E. W. McFarland, Size- and support-dependent electronic and catalytic properties of Au⁰/Au³⁺ nanoparticles synthesized from block copolymer micelles. *J. Am. Chem. Soc.* 125, 12928-12934 (2003)
38. S. A. Sardar, T. F. Jaramillo, L. G. Cameron, M. M. Sushchikh, and E. W. McFarland, UV-light induced sintering behavior of Au nanoclusters. In *American Chemical Society Meeting*, 2005; Vol. 229, p U988
39. J.-P. Zhang, D. T. Foord, J. Chou, and E. W. McFarland, Direct evidence of shelled structures of Au-Pd bimetallic nano-particles. *Microscopy & Microanalysis* 11, 1468-1469 (2005)
40. W. Tang, L. H., A. Kleiman-Shwarsstein, G. D. Stucky, and E. McFarland, Size-dependent activity of gold nanoparticles for oxygen electro-reduction in alkaline electrolyte. *J. Phys. Chem.* submitted (2008)
41. X. Liu, T. F. Jaramillo, A. Kolmakov, S.-H. Baeck, M. Moskovits, G. D. Stucky, and E. W. McFarland, Synthesis of Au nanoclusters supported upon a TiO₂ nanotube array. *J. Materials Research* 20, 1093-1096 (2005)
42. Y. Yang and E. W. McFarland, Stability study of highly dispersed Au clusters produced on sputter defected TiO₂(110): Evidence from SEM and olefin TPD. *Proc. Mater. Res. Soc.* 854, paper number U5.2 (2004)

43. M. Sushchikh, J. Colby, L. Cameron, W. Tang, A. Kleiman-Shwarscstein, J. N. Park, H. Metiu, and E. W. McFarland, Design and construction of a batch microreactor for investigations of heterogeneous catalysts deposited on flat supports. *Surface Science*, to be submitted (2008)
44. M. Sushchikh, L. Cameron, H. Metiu, and E. McFarland, Size and pressure independent kinetics of CO oxidation on alumina supported iridium. *Res. Let. Phys. Chem.*, submitted (2007)
45. Y. Yang, M. Sushchikh, G. Mills, H. Metiu, and E. W. McFarland, Reactivity of TiO₂ with hydrogen and deuterium. *Applied Surface Science* 229, 346-351 (2004)
46. A. Kolmakov, D. Klenov, Y. Lilach, S. Stemmer, and M. Moskovits, The effect of Pd doping on the sensing properties of individual SnO₂ nanowires. *Nano Lett.* 5, 667-673 (2005)
47. A. Kolmakov and M. Moskovits, Chemical sensing and catalysis by one-dimensional metal oxide nanostructures. *Ann. Rev. Mater. Res.* 34, 151-180 (2004)
48. A. Kolmakov, Y. Zhang, G. Cheng, and M. Moskovits, Detection of CO and O₂ using SnO₂ nanowire sensors. *Adv. Mater.* 15, 997-1000 (2003)
49. A. Kolmakov, Y. Zhang, and M. Moskovits, Topotactic thermal oxidation of Sn nanowires: intermediate suboxides and core-shell metastable structures. *Nano Lett.* 3, 1125-1129 (2003)
50. Y. Zhang, A. Kolmakov, S. Chrétien, H. Metiu, and M. Moskovits, Control of catalytic reactions at the surface of a metal oxide nanowire by manipulating electron density inside it. *Nano Letters* 4, 403-407 (2004)
51. Y. Zhang, A. Kolmakov, Y. Lilach, and M. Moskovits, Electronic control of chemistry and catalysis at the surface of an individual tin oxide nanowire. *J. Phys. Chem. B* 109, 1923-1929 (2005)
52. S. Dmitriev, Y. Lilach, B. Button, M. Moskovits, and A. Kolmakov, Nanoengineered chemiresistors: the interplay between electron transport and chemisorption properties of morphologically encoded SnO₂ nanowires. *Nanotechnology* 18, art. no. 055707 (2007)
53. S. V. Kalinin, J. Shin, S. Jesse, D. Geohegan, A. P. Baddorf, Y. Lilach, M. Moskovits, and A. Kolmakov, Electronic transport imaging in a multiwire SnO₂ chemical field-effect transistor device. *J. Appl. Phys.* 98, art. no. 044503 (2005)
54. Y. Lilach, J.-P. Zhang, M. Moskovits, and A. Kolmakov, Encoding morphology in oxide nanostructures during their growth. *Nano Lett.* 5, 2019-2022 (2005)
55. M. Moskovits, D.-H. Jeong, T. Livneh, Y. Wu, and G. D. Stucky, Engineering nanostructures for single-molecule surface-enhanced Raman spectroscopy. In *Nanosensing: Materials and Devices (Proc. SPIE 5593)*, M. S. Islam; A. K. Dutta, Eds. (2004); pp 478-490
56. M. Moskovits, D.-H. Jeong, T. Livneh, Y. Wu, and G. D. Stucky, Engineering nanostructures for single-molecule surface-enhanced Raman spectroscopy. *Israel Journal of Chemistry* 46, 283-291 (2006)
57. J. P. Schmidt, S. E. Cross, and S. K. Buratto, Surface-enhanced Raman scattering from ordered Ag nanocluster arrays. *J. Chem. Phys.* 121, 10657-10659 (2004)
58. Y. Wu, G. Cheng, K. Katsov, S. W. Sides, J. Wang, J. Tang, G. H. Fredrickson, M. Moskovits, and G. D. Stucky, Composite mesostructures by nano-confinement. *Nature Materials* 3, 816-822 (2004)

59. Y. Wu, T. Livne, Y. Zhang, G. Cheng, J. Wang, J. Tang, M. Moskovits, and G. D. Stucky, Templated synthesis of highly ordered mesostructured nanowires and nanowire arrays. *Nano Lett.* 4, 2337-2342 (2004)
60. H. Metiu, Preface: Recent developments in density functional theory: Orbital dependent functionals. *J. Chem. Phys.* 123, art. no. 062101 (2005)
61. E. S. Baker. *From Solution to a Solvent Free Environment: Probing The Structures of Noncovalently Bound DNA and RNA Complexes*. Ph. D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2005)
62. L. A. Benz. *Deposition and Investigation of Mass Selected Gold and Silver Clusters on a Titanium Dioxide (110) Surface: Preparation of a Model Catalyst*. Ph. D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2007)
63. D. Gargas. *Investigation of Porous Silicon Properties for Applications in Microphotonics and Electrochemical Nanolithography*. Ph.D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2007)
64. T. F. Jaramillo. *Photoelectrochemical Hydrogen Production: The Investigation of Improved Material Compositions and Morphologies Utilizing a Combinatorial Electrochemistry Methodology*. Ph. D. dissertation, Chemical Engineering, University of California, Santa Barbara (2004)
65. M. J. Manard. *Exploring the Gas Phase Properties of Coinage Metal Clusters and their Interactions with Small Alkenes*. Ph.D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2006)
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67. E. L. Orazem. *Raman Spectroscopy on the Nanoscale: An Investigation of Silver Triangle Arrays, Polymer Laminates and Gold-Loaded Mesoporous Titania Films*. Ph.D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2007)
68. J. P. Schmidt. *Probing Molecular Interactions at the Nanoscale with Single Molecule Spectroscopy and Surface-Enhanced Raman Scattering*. Ph.D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2003)
69. D. J. Sirbulu. *Probing and Manipulating the Optical Properties of Porous Silicon: Films, Nanoparticles, and Microstructures*. Ph.D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2003)
70. M. Sushchikh. *Investigations of Hydrocarbon Reactions on Iridium Surfaces*. Ph.D. dissertation, Chemical Engineering, University of California, Santa Barbara (2006)
71. B. Temel. *Applications of Computational Quantum Mechanics*. Ph.D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2006)
72. S. A. Varganov. *Cool Clusters Correctly Correlated*. Ph.D. dissertation, Chemistry, Iowa State University (2005)
73. Q. Zhang. *Mass Spectrometry Studies on Methane Activation and Sea Salt Dissolution in the Gas Phase: Energetics and Mechanics*. Ph.D. dissertation, Chemistry & Biochemistry, University of California, Santa Barbara (2003)